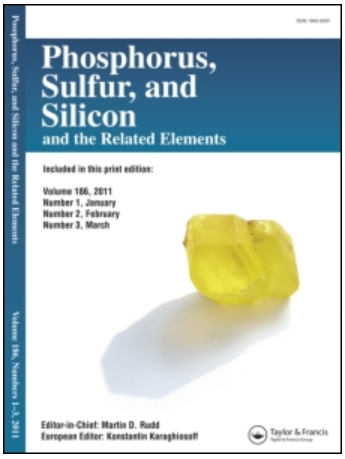

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Functionalisation of 2 Halophosphinines

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FUNCTIONALISATION OF 2 HALOPHOSPHININES.

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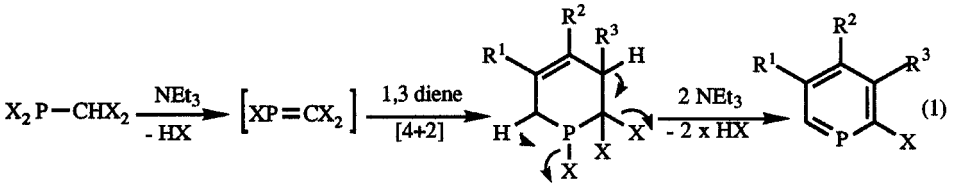
Abstract

Some recent developments in the chemistry of phosphinines are discussed. They include a one pot synthesis of C- polybrominated phosphinines through direct bromination of the phosphinine ring and a preliminary investigation of the reactivity of these species.

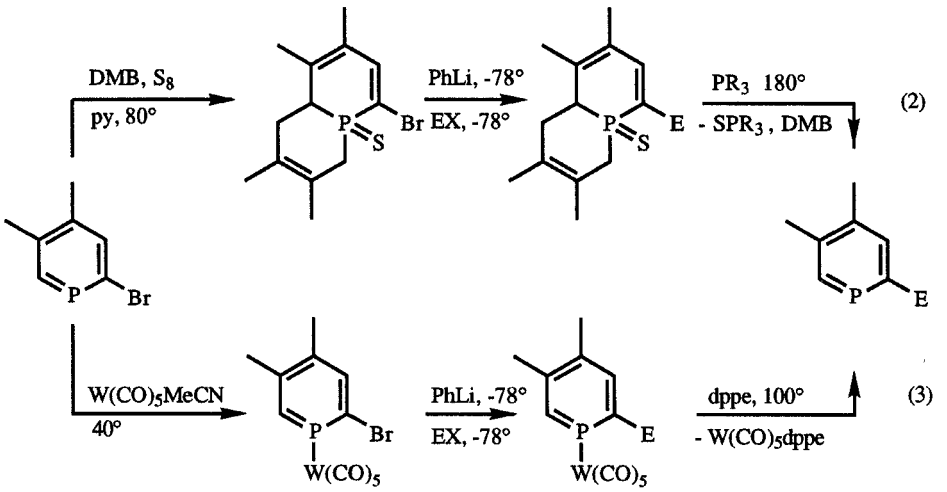
It is 25 years since the discovery of phosphinines, so they are clearly no longer exotic from a synthetic standpoint. Furthermore, since they have no uses at the present time, they have reached a crucial point in their development. Coordination chemistry is potentially one of their most important applications, but it can only become truly viable if a wide range of interesting ligands is readily available. Thus, techniques which allow the convenient synthesis and derivatisation of phosphinines are clearly imperative.

Functionalised phosphinines are known, but substituents have to be introduced by rather specific and complicated procedures; a survey of the literature shows that no general method for grafting functional groups onto a preformed phosphinine ring is available. As a first step towards an easy access to functionalised structures, we developed a simple one- pot synthesis of 2- halophosphinines[2,3].Eq. (1).

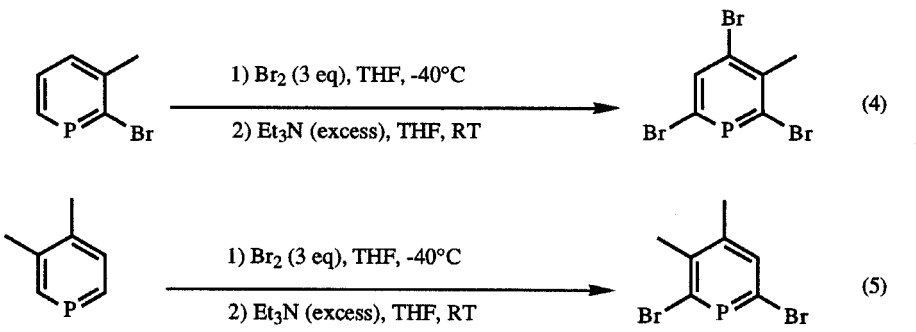


R = Me, H; X = Cl, Br

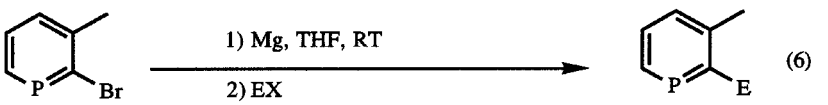
Unfortunately, the direct functionalisation of the carbon in the 2- position proved to be difficult, because of the high reactivity of the P=C double bond towards metallating agents. However, we were able to develop two pathways which used 'masked' synthetic equivalents of 2- lithiophosphinines. After reversibly protecting the P=C bond, either by complexation of the phosphorus lone pair to [M(CO)5] (M = Cr, Mo, W) Eq. (3), or through 2 + 4 cycloaddition with sulfur and a conjugated diene Eq. (2), it was possible to synthesise several 2- functionalised phosphinines[4]. Amongst these is the first example of a 2, 2' biphosphinine, the phosphorus analogue of bipyridine[5,6].



In the light of these advances, it was important to open up the chemistry of more complicated species such as 2,6 di- and 2,4,6 tri- functionalised phosphinines. These require a synthesis of polybrominated phosphinines, which we prepare in a one step reaction, directly from 2-bromo or 2,6- unsubstituted phosphinines Eqs (4) and.(5).



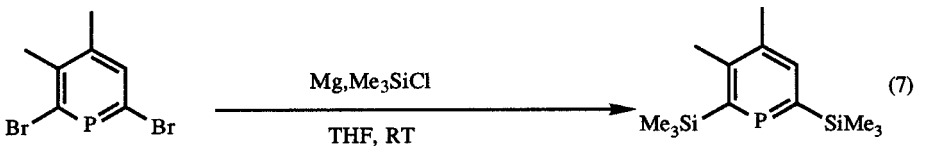
For their functionalisation, we first tried to duplicate the pathway which was successfully used with 2- bromophosphinines. However, difficulties were encountered with the corresponding lithio derivatives, which are disappointingly unreactive. Fortunately, a reinvestigation of the behaviour of 2- bromophosphinine towards magnesium allowed the problem to be resolved. Previously, we had found that the corresponding, stable, Grignard reagents were difficult to generate efficiently, because of their tendency to react with excess bromophosphinine to give polymeric material. In situ trapping of the Grignard reagent with good electrophiles naturally proved to be successful, with some interesting 2- functionalised phosphinines being synthesised in good yields[7] Eq. (6).



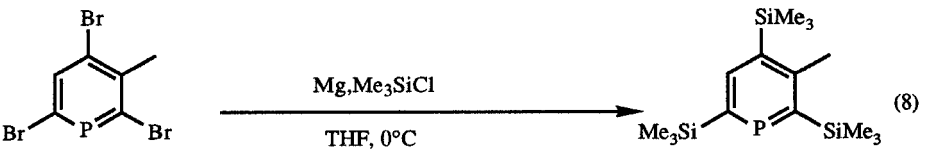
(6)

E = $SiMe_3Cl$, $SiMe_2Cl$, $SiMe_2H$, $SnMe_3$.

The route outlined above works well for 2,6 dibromo- and 2,4,6 tribromo-phosphinines, which display greater reactivity than the monohalophosphinines Eqs. (6) and (7).The formation of the tris(trimethylsilyl)phosphinine is particularly interesting, as is the synthetic potential of the corresponding trimethylstannane.

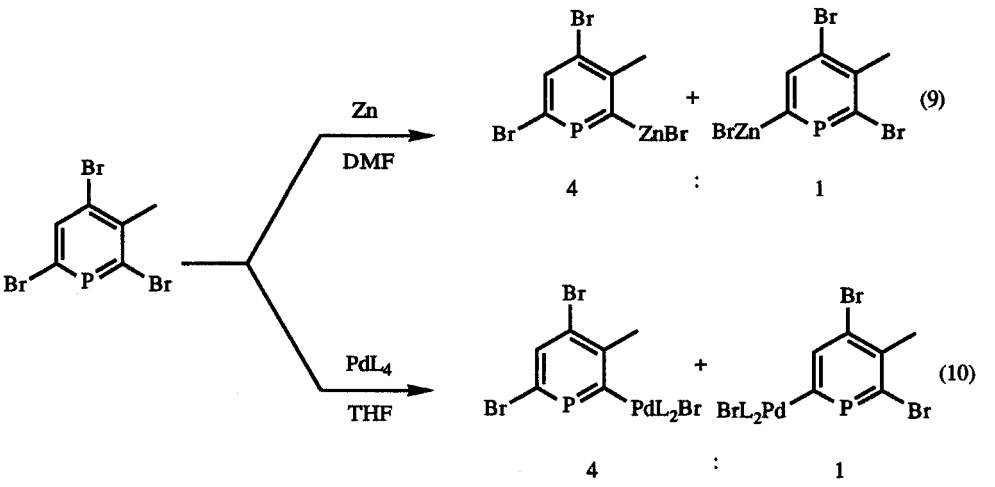


(7)



(8)

These encouraging results with magnesium prompted us to investigate if other metallic fragments could interact with the highly reactive carbon-bromine bond of 2,4,6 - tribromophosphinines.In further experiments we have recently discovered an access to Zinc[8] and Palladium derivatives of phosphinines Eqs. (9) and (10).



At present, the study of these interesting metallic derivatives, and their synthetic potential, is continuing.

REFERENCES

1. G Märkl, 'Phosphinines', in 'Multiple bonds and low coordination in Phosphorus Chemistry', M Regitz and O J Scherer, (Eds.), Thieme Verlag, Stuttgart, 1990.
2. P Le Floch, F Mathey, Tet .Lett., (1989), 30, 817.
3. P Le Floch, L Ricard, F Mathey, Polyhedron, (1990), 9, 991.
4. P Le Floch, D Carmichael, L Ricard, F Mathey, Organometallics, (1991), 10, 2432.
5. P Le Floch, D Carmichael, L Ricard, F Mathey, J.Am.Chem.Soc, (1991), 113, 667.
6. P Le Floch, D Carmichael, L Ricard, F Mathey, A Jutand, C Amatore, Organometallics, accepted for publication.
7. P Le Floch, D Carmichael, F Mathey,Bull. Soc. Chim. France, accepted for publication.
8. A Zinc derivative of a 2-iodophosphinine has been recently synthesised. see H.T.Teunissen, F. Bickelhaupt, Tet .Lett, (1992), 33, 3537.